RESEARCH ARTICLE

Use of Hen Feathers as a Potential Biosorbent for the Removal of Malachite Green

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ABSTRACT: Waste material, hen feather, a biosorbent was successfully utilized in removing a water-soluble hazardous Malachite Green Dye. The study incorporates the effect of parameters time, initial concentration, adsorbent dosage, pH, temperature. The adsorption data validates up to 99.80%of the malachite green dye was biosorbed at 303 K demonstrating the biosorbent potential of the waste (hen feathers)for the removal of malachite green dye. The results indicated that the maximum biosorbent removal can be achieved at 4 of pH value and equilibrium can be reached in 60 minutes. The Freundlich Isotherm model provides better desorption for the adsorption equilibrium when compared with the Langmuir Equation in the conditions of the present study. Based on these isotherms, Thermodynamic parameters like Gibbs free energy change in enthalpy, and entropy was calculated. Kinetics of the ongoing adsorption was also monitored. The specific rate constant for the involved process was calculated at different temperatures. Kinetic measurements suggest 2nd order adsorption kinetics. This work showed that the biosorbent hen feathers a waste material can be effectively used for the removal of Malachite Green Dye from its aqueous solutions.

KEYWORDS: Hen feather; Malachite Green dye; Adsorption; Isotherms; Kinetics.

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1. INTRODUCTION

Water pollution caused to the discharge of colored effluents from textile dye manufacturing and textile dyeing mills is one of the main environmental concerns within the world today. Though dyes impart appealing colors to textile fibers, foodstuffs, etc., however, strong colors imparted by the dyes pose aesthetic and ecological problems to the aquatic ecosystems. Because of their complex molecular structures and enormous sizes, most of the dyes are considered non-oxidizable by conventional physical and biological treatments [1]. Thus their decolourisation is one among the indispensable processes in wastewater treatment. Several techniques aimed at preferential removal of different types of dyes from wastewater have been developed [2,3]. Among these physicochemical methods like adsorption[4,5], electrochemical coagulation [6] and photocatalytic decolourisation [7] are more popular nowadays. Among all these, adsorption is one of the methods, which is gaining more and more attention because of its easy operations and versatility. It is a useful and straightforward technique and allows kinetic and equilibrium measurements with none highly sophisticated instrument[8]. Consequently, various potential adsorbents are implemented for the removal of specific organics from water.

Ever since the adsorption technique has been used for the removal of toxic chemicals from wastewater there has been a struggle to uncover some new, economic, and competent adsorbents, particularly waste materials. Thus, many waste materials like, shells, husks, plant leaves, etc., have been tried as adsorbents. But still, the question mark on the economics involved in the developed process persists. Moreover, most of these materials are also utilized for some other useful purposes and this makes their availability difficult. Recently, our laboratory explored the use of waste material, hen feathers, as biosorbent to remove a toxic triphenylmethane dye, Malachite green dye, and found these quite proficient and economic.

The dye under consideration is Malachite Green, which is an important water-soluble dye belonging to the triphenylmethane family. The available toxicological information reveals that in the tissues of fish and mice Malachite Green easily reduces to

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Leucomalachite Green [9], [10], which acts as a tumor promoter. Thus, the detection of Malachite Green in fishes, animal milk, and another foodstuff, destined for human consumption, alarm the health hazards against human beings[11,12]. Studies also confirm that the products formed after degradation of Malachite Green are also not safe and have the carcinogenic potential[13]. Keeping the toxicity of Malachite Green in view various attempts have been made for its removal from the waste water. But most of these materials are either costly or useful for other purposes, while hen feather is an easily available waste material, which can be obtained at negligible cost.

The present study is devoted to dye removal from the wastewater using the adsorption technique. The study has been carried out under different variables like time, initial concentration, adsorbent dosage, pH, and temperature. And a convenient and economically viable process has been developed by involving a waste material- hen feathers as a potential adsorbent.

2. MATERIALS AND METHODS

2.1 Preparation of the biosorbent

Collected hen feathers were of about 1 cm length, which was first agitated and rinsed thoroughly in the pool of doubly distilled water and then dried. Soft barbs of every dried feather were now cut into small pieces of about less than 0.1mm length and hard middle rachis was removed and discarded. Barbs were then treated with hydrogen peroxide (30%, v/v) for about 24 h to oxidize the adhering organic material. The material thus obtained was kept in an oven at 100^{0}Cfor 12 h for the removal of moisture and finally stored in a vacuum desiccators [13].

2.2 Characteristics of the biosorbent

The biosorbent characterization was done by employing a spectrum GX spectrophotometer from 400-4000 cm with a resolution of 1/cm using four scans with background subtraction. The peaks were noted from the spectra by comparing it with literature reported spectra.

2.3 Preparation of dye solution

The Malachite green dye was obtained from Ranbaxy laboratories limited (India) and used without further purification. A stock solution of 1000 mg L-1 was prepared by dissolving 1 g of dye in 1000 ml of double-distilled water which was later diluted to the specified concentrations. All the solutions were prepared using double water. Solution pH was adjusted by adding HCl and NaOH as needed. Concentrations of the dye solutions were determined from the absorbance of the solution at the characteristic wavelength (λ_{max} = 620nm) of MG employing double beam UV-Visible spectrophotometer. Samples were diluted if absorbance exceeds 3. Final concentrations were determined from the calibration curve [14].

2.4 Equilibrium Studies

A volume of 50mL of MG solutions at the desired concentration was introduced into 150mL conical flasks. 0.3g of Hen Feathers was added to the solutions. The flasks were agitated on a shaker at 150 rpm at a constant temperature. Samples were taken from the mixture during stirring at predetermined time intervals to determine the residual MG concentration in the system. Samples were centrifuged and the supernatant liquid was analyzed for the remaining color. All the experiments were carried out twice in parallel and average values were calculated further. For isotherms studies, a series of flasks containing 100mL of MG solution in the range of 40-360 mg·L^{-1} was prepared. Hen Feathers (0.3g) was added to each flask and then the mixtures were agitated at 25, 30, 35, 40 and 45 ^{0}C, respectively, for 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60 minutes [15].

2.5 Adsorption & Kinetic Studies

All adsorption measurements were carried out through batch technique at 30, 40, and 50 ^{0}C temperatures and desired pH. In each measurement, 25 mL of the dye solution of the desired concentration and appropriate amount of Hen Feathers were taken in a 100 mL graduated airtight conical flask and mechanically agitated intermittently for about 2 – 4 hours to achieve equilibrium. However, in the case of kinetics measurements, the flask was shaken only for the desired time period. The feathers were now removed from the solution after carefully filtering by Whatman filter paper No. 42 and the concentration of the dye was determined spectrophotometrically by recording the absorbance at λ_{max} 520 nm [15].

3. RESULTS AND DISCUSSION

3.1 FT-IR measurements for Malachite Green treated Hen Feathers

Infrared spectroscopy belongs to the group of molecular vibration spectroscopy's which are molecule-specific and give direct information about the functional groups, their kind of interactions, and orientations. Its sampling requirements allow the gain of information from liquids/gases and in particular from solid surfaces. The shift of bands and changes in signal intensity allows the identification of the functional groups involved in dyesorption.

FT-IR measurements for MG dye loaded with Hen Feathers are shown in Fig. 1.The peaks at 680 cm^{-1} indicate Alkyl halides (C-Cl). The peak at 1465 cm^{-1} indicates Alkyl C-H stretch mode. The peak at 3217 cm^{-1} indicates Asymmetric -CH_2-, Symmetric CH_3 and -CH_2 stretching vibrations. The peak at 3286 cm^{-1} indicates the Amine N-H group. The bands at 3759 cm^{-1}, 3801 $cm^{-1,}$ and 3817 cm^{-1} indicate Non bonded O-H stretch Hydroxyl group. The peak at 3992 cm^{-1} indicates the O-H group as well as Amine N-H stretch modes

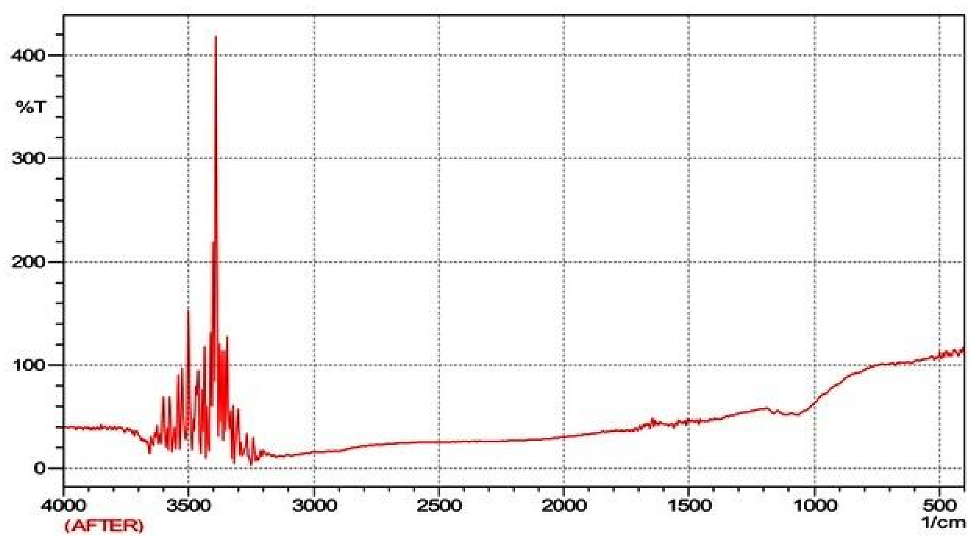

Figure-1 FT-IR plot after activation

3.2 Equilibrium Studies on Malachite Green by Hen Feathers powder

3.2.1 Effect of contact time

Time-course profiles for the adsorption of Malachite Green from a solution of concentrations ranging from 20-100 mg L^{-1} are shown in Fig2 and 3. The data obtained from the adsorption of Malachite Green dye on the usedshowed that a contact time of 60 min was required to achieve equilibrium adsorption and there was no significant change in concentration of the dye with further increase in contact time for all concentrations of Malachite Green solution. Therefore, the amount of dye uptake and the amount of color removed at the end of 60 min were given as the equilibrium value, Q_{eq} = 3.192 (mg g^{-1}) and C_{eq} = 0.77(mgL^{-1}).The rapid uptake at the initialtime period was obtained presumably because initially, all theactive sites were unoccupied and readily available for the sorption ofa large amount of dye ions from the solution phase [16]. For further studies of adsorption with other variable parameters, the equilibrium time of 60 min has been chosen as the optimum time.

3.2.2 Effect of Initial Concentration

From the Fig-4, it was observed that the percentage of dye removal showed a decreasing trend as the initial MG concentration increased from 20 to 100 mg L-1. At lower concentrations, all the MG present in the adsorption medium could interact with the binding sites and hence higher percentage of dye removal has observed as shown in Fig-4. At higher concentrations, a lower percentage of dye removal was observed because of the saturation of the adsorption sites. With an increase in initial MG concentration from 20 mg L-1 to 100 mg L-1, dye uptake was increased from 3.19 mg g-1 to 14.53 mg g-1, and the percentage of dye removal decreased from 96.15 % to 87.53%. Similar trends were also reported by Alok Mittal [17] in his kinetic and equilibrium studies of Malachite Green by Hen Feathers.

3.2.3 Effect of solution pH

Initial pH is one of the most important factors affecting the adsorption process. Fig. 5 and 6 show the effect of initial pH on the adsorption of Malachite Green onto *Hen Feathers*. The percentage of dye removal was increased from 91.05% to 96.45% and dye uptake was increased from 3.02 mg g^{-1} to 3.20 mg $g^{-1}$for 20 ppm with an increase in pH from 2 to 4 and there onwards the values decreasing with an increase in pH up to 9. Hence optimum pH was taken as 4. At lower pH, both the hydrogen ions as well as Malachite Green ions compete together resulting in less

adsorption. As the pH increases, the amount of OH^- ions increases which leads to the electrostatic attraction of the positive Malachite Green ions with that of negative ions on the adsorbent thereby % of adsorption increases. Similar trends were also reported by Alok Mittal et al[17].

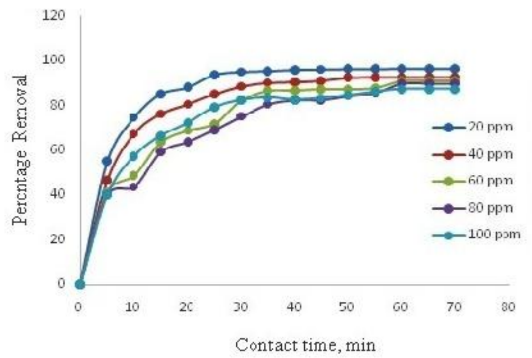

Figure-2:Effect of Contact Time on Percentage Removal

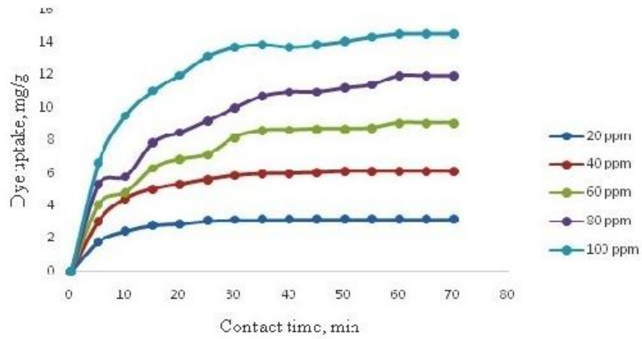

Figure-3: Effect of Contact Time on Dye uptake

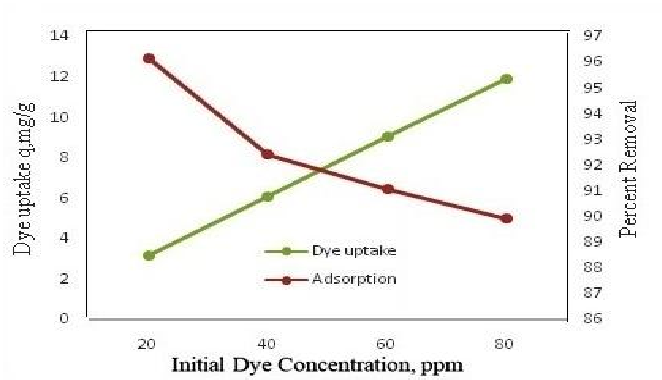

Figure- 4: Effect of Initial Concentration on % Removal & Dye Uptake

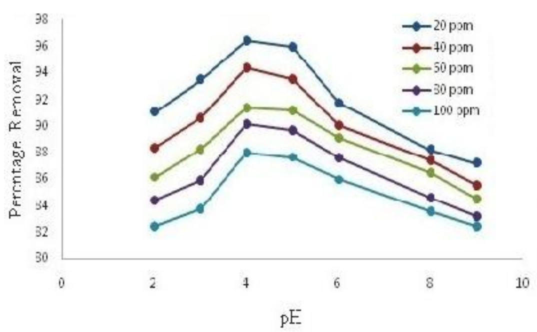

Figure-5: Effect of pH on Percentage Removal

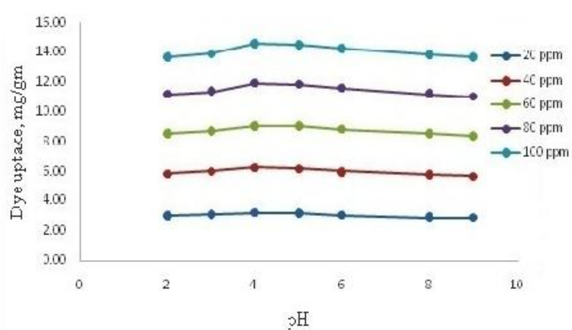

Figure-6: Effect of pH on dye Uptake

3.2.4 Effect of Temperature

Figures 7 & 8 represents the effect of temperature on % removal of malachite green and dye uptake using hen feather powder as an adsorbent. When the adsorption was carried out at five different temperatures from 298 to 333 K for concentrations ranging from 20 to 100 mg L^{-1}, the extent of adsorption improved steadily with an increase in adsorption temperature. The Malachite Green

adsorption on the Hen Feathers powder was endothermic. When the adsorption is endothermic, an increase in temperature results in an increase in K_D. This indicated a shift of the adsorption equilibrium to the adsorption direction. An increase in temperature is followed by an increase in diffusivity of dye ion, and consequently by an increase in the adsorption rate of diffusion is the rate-controlling step. The amount of dye uptake was increased in Fig.8 from3.14 mg g^{-1} to 14.11 mg g^{-1} for a temperature rise of (298-333 K). This increase in binding could be due to an increase in surface activity and increased kinetic energy of the dye molecules [18].

3.3 Kinetic studies

Experiments were conducted with different concentrations of Malachite green dye with a pH of 4 with the temperature of 303 K at 180 rpm agitation speed to identify the mechanism of Malachite Green biosorption using Hen Feathers as biosorbent. The results were obtained shown in Fig. 9 for Malachite Green respectively.

From this figure, it was found that the second-order was fitted for entire range concentrations of studied for dye (R2= 0.99). The pseudo-second-order kinetics describes the mechanism of Hen Feathers powder is better compared to the first-order kinetics. In the pseudo-second-order model, the regression values from the graph are very good and the error between the Dye uptake (Qeq) model and Dye uptake (Qeq) experimental is minimum. Thus, from these values, it was suggested that pseudo-second-order kinetics was the best fit for this data.

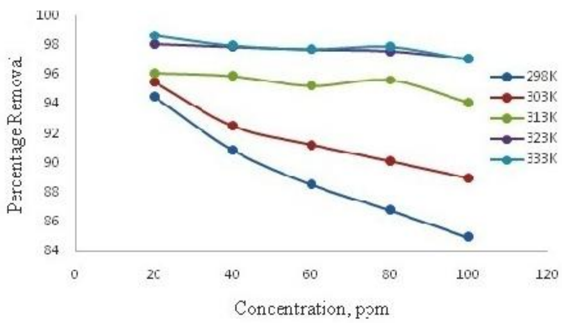

Figure- 7: Effect of Temperature on Percentage Removal

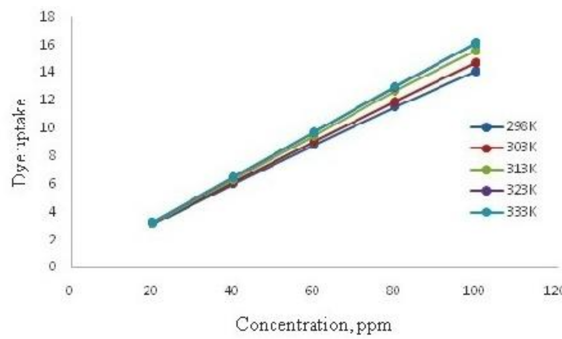

Figure- 8: Effect of Temperature on Dye uptake

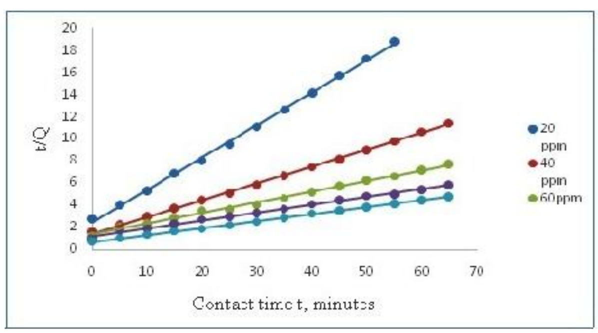

Figure- 9: Second order kinetics for adsorption of Malachite Green using Hen Feathers

3.4 Biosorption isotherm models

3.4.1. Langmuir isotherm

The Langmuir isotherm [17] has been successfully applied to many pollutant adsorption processes and has been the most widely used adsorption isotherm for the adsorption of a solute from a liquid solution. A constant assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that when a dye molecule occupies a site, no further adsorption can happen at that site. The rate of adsorption to the surface should be proportional to a driving force, which times an area. The driving force is the concentration in the solution, and the area is the amount of bare surface.The

Langmuir nonlinear equation is commonly expressed as followed:

$$Q_{eq}=\frac{Q_{\max}bC_{eq}}{1+bC_{eq}} \quad (1)$$

The above equation (1) can be rearranged to the following linear form:

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{bQ_{\max}} + \frac{1}{Q_{\max}} C_{eq} \quad (2)$$

A plot of Ce/qe versus Ce should indicate a straight line of slope 1/Qmand an intercept of 1/(KaQm).

The calculated K_R value in the present study indicated that adsorption is lower at low concentrations of Malachite Green than higher concentrations. Therefore, Hen Feathers would be not an effective adsorbent for removing Malachite Green from solution Fig.10.

3.4.2 Freundlich isotherm

The Freundlich isotherm model [20]is the earliest known equation describing the adsorption process. It is an empirical equation and may be used for non-ideal sorption that involves heterogeneous adsorption. The Freundlich isotherm can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites and is commonly given by the following non-linear equation.

$$Q_{eq}=K_fC_{eq}^{m} \quad (3)$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log Q_{eq} = \log K_f + m \log C_{eq} \quad (4)$$

A plot of log Q_{eq}vslogC $_{eq}$ gives a slope of 1/m and intercept of logKf. Freundlich isotherm is derived assuming heterogeneity surface. K_f and m are indicators of adsorption capacity and adsorption intensity. For favorable adsorption the value of ‘m’ should be in between 1-10.

From Freundlich isotherm, the constants related to the adsorption coefficient (K_f) and intensity (m) were estimated as 3.5678 (favorable), 1.7489 for Malachite Green solution Fig.11.

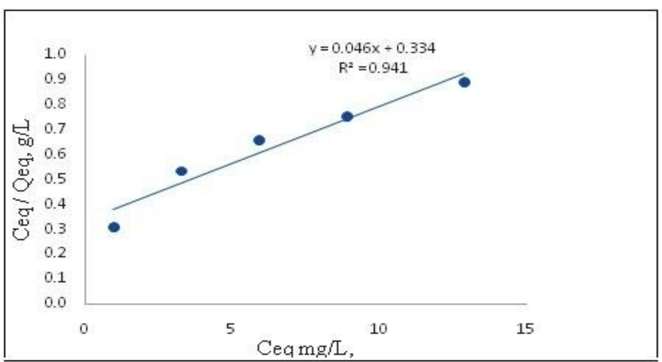

Figure- 10: Langmuir Isotherm for adsorption of Malachite Green using Hen Feathers

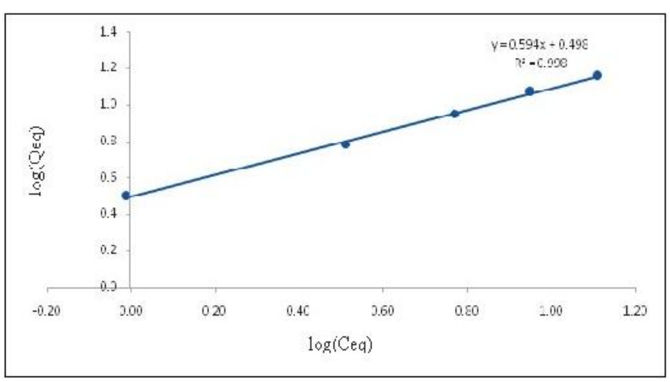

Figure- 11: Freundlich Isotherm for adsorption of Malachite Green using Hen Feathers

3.4.3 Temkin Isotherm

Tempkin adsorption isotherm model was used to evaluate the adsorption potentials of the Hen Feathers for MG. The derivation of the Tempkin isotherm assumes that the fall within the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Tempkin isotherm has commonly been applied in the following form [21]:

$$q_{eq} = \frac{RT}{b_T} \ln(A_T C_{eq}) \tag{5}$$

This can be written as,

$$q_{eq} = \frac{RT}{b_T} \ln C_{eq} + \frac{RT}{b_T} \ln A_T . \tag{6}$$

An adsorption isotherm is characterized by certain constants, the values of which express the surface properties and affinity of the sorbent and can be used to compare the adsorptive capacity of adsorbent for different dyes. Temkin isotherm constants A_t and b_t were found to be 1.358 and 255.71 in Fig.12.

3.5 Thermodynamic studies

Thermodynamic parameters such as Enthalpy change (ΔH^o), free energy change (ΔG^o) and entropy change (ΔS^o) can be estimated using equilibrium constants changing with temperature. The free energy change of the sorption reaction is given by the following equation:

Where,

$$\Delta G^o = -RT \ln K_a \tag{7}$$

ΔG^0 is the standard free energy change, J/mol.
R is the universal gas constant, 8.314 $J mol^{-1} K^{-1}$ and
T is the absolute temperature, Deg K.

The equilibrium constant may be expressed in terms of enthalpy change of adsorption as a function of temperature as follows:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^0}{RT^2} \tag{8}$$

According to Eq. (8), the effect of temperature on the equilibrium constant K_a is determined by the sign of ΔH^o.

The integrated form of Eq. (8) becomes

$$\ln K_a = \frac{-\Delta H^0}{RT} + \Delta S \tag{9}$$

Eq (9) can be rearranged to

$$-RT \ln K_a = \Delta H^o - TR \Delta S \tag{10}$$

Where ΔS^0 is, the change with temperature of the free energy change with temperature and the equilibrium constant can be represented as follows:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{11}$$

$$\ln K_a = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{12}$$

Eq (12) shows clearly that the adsorption process is composed of two contributions, enthalpic change and entropic, which characterize whether the reaction is spontaneous. The free energy change for Malachite Green dye

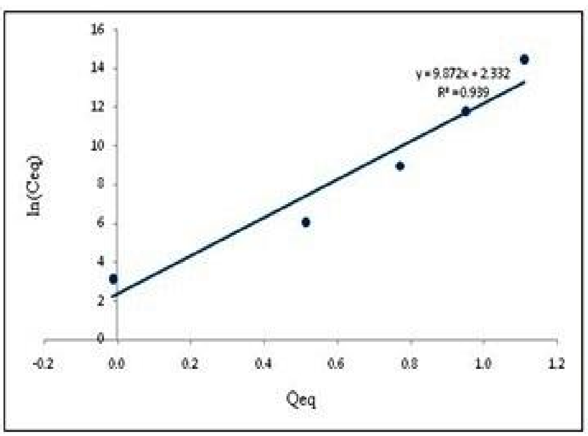

Figure-12:Tempkin Isotherm for adsorption of Malachite Green using Hen Feathers

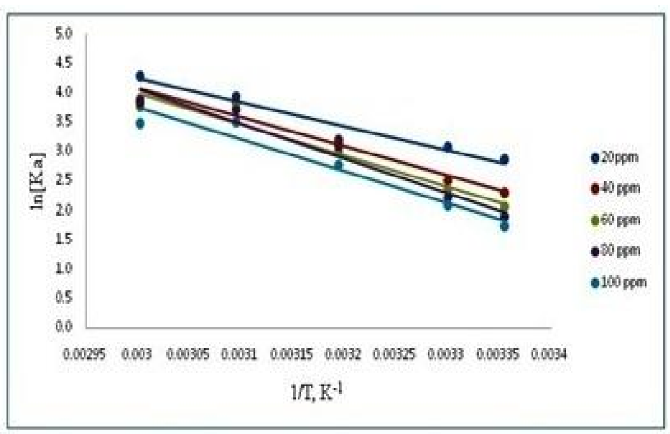

Figure- 13: Van't Hoff plot

4. CONCLUSION

The present work helped in identifying a new source of the adsorbent for the removal of dyes from effluent wastes containing low concentrations of dyes. The adsorption performance is strongly affected by parameters such as agitation time, initial dye concentration, pH, adsorbent dosage, and temperature. The percentage adsorption of Malachite Green was increased with an increase in contact time. The equilibrium uptake was decreased and percentage adsorption was increased with an increase in the adsorbent dosage. The plot of pH versus percentage removal of dye showed that the significant adsorption took place at a pHvalue of 4. The percentage adsorption of Malachite Green was decreased with an increase in the initial dye concentration and dye uptake was increased substantially. The percentage adsorption of Malachite Green was decreased with an increase in the temperature. Hence this indicates that this process is chemisorption.The dye removal data of Malachite Green follows the Freundlich model with the best fit with Adsorption Coefficient, K_f= 3.5678, and R^2= 0.9982.The kinetics of the adsorption of Malachite Green on *Hen Feathers* can be better described with pseudo-second-order kinetics. The present work helped in identifying a new source of the adsorbent for the removal of dye from effluent waste containing a low concentration of dyes. The results obtained in these studies open perspectives with relation to the utilization of *Hen Feather powder* in the removal of Malachite Green in the treatment of wastewater from textile industrial effluents.

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